Solid State Chemistry.
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Lecture – 42
Geometric Structure Factor – Missing Peaks

Now, I will start the second lecture of week 9 of this course. In this lecture I will continue the discussion on Geometric structure Factor ok, and we will I will show in detail how to calculate the geometric structure factor for any crystal ok. So, week 9 lecture 2 will be geometric factor I will also talk about the Missing Peaks in crystal structure in an xrd pattern ok.

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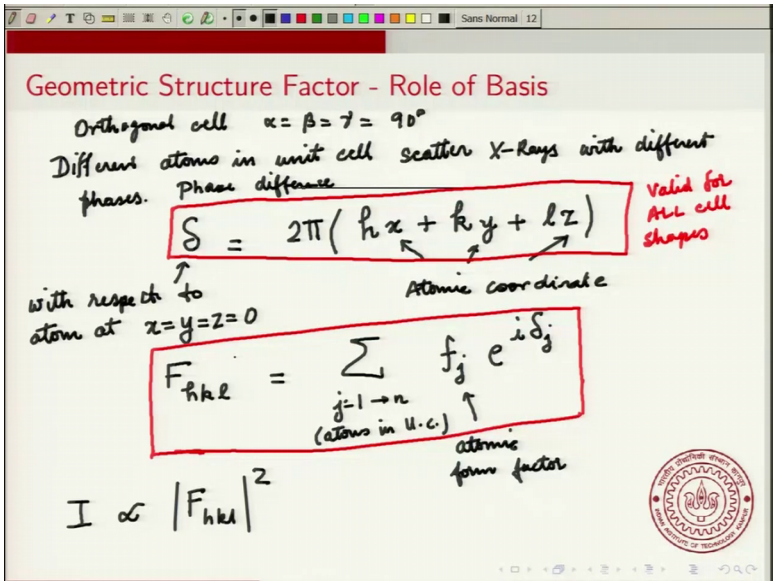

So, geometric factor basically kills the role of the basis ok. And here if you take an orthogonal cell for example, if you take an orthogonal cell that is alpha equal to beta equal to gamma equal to 90 degrees. So, if you take such a cell then the different, so the different atoms in the cell, in unit cell so, they scatter with different phases scatter X-rays with different phases ok.

So, this is similar to when we when we talk about the Bragg's scattering wheats we said that there is a phase difference between the different X-rays falling on different lattice planes ok. Here we are talking about the phase difference between the X-ray scattered by different atoms of a unit cell. And this phase difference delta, so the phase difference

delta, delta is given by this expression 2 pi h times x plus k times y plus l times z ok. x, y and z are the coordinates of the atom within the unit cell. So, xyz are or the coordinates of the atom ok. And this phase difference delta is with respect to atom at x, x equal to y equal to z equal to 0. So, this is phase difference with respect to the atom of the origin. So, clearly if I put x, y, z, 0 ok; then the delta will be 0. So, this delta is with respect is the phase difference of an atom located at x, y, z with respect to the atom located at the origin.

So, what is the role of this phase difference? So obviously, this phase difference will lead to interference and this incidentally, I should mention that this expression can be used for all unit cell shapes ok. Not just orthogonal unit cell; so valid for all cell shapes ok. it is most easily seen in the case of orthogonal cells, but this is in general valid for all cell shapes ok.

So now, how does this affect the geometric structure factor? So, the geometric structure factor F for h hkl ok. So, the geometric structure factor form for the scattering from the hkl plane ok, is given by sum over all j equal to 1 to n, these are the atoms in the atoms in the cell unit cell ok. f j, so that is the atomic form factor, times e to the i delta of the j th atom. So, delta is the is the phase difference of the j th atom ok. And this is the formula for the geometric structure factor and let me also put this in a box because this formula is very crucial ok.

And, you can and the relevance of this a f is that the intensity is proportional to f hkl square ok. So, the intensity is proportional to square of this scattering factor ok. So, therefore, if the scattering factor is 0, for some for some value of hkl; then the intensity of that peak will be 0 ok. Even though it satisfies the Bragg's scattering condition. So, this is the structure factor that remember the structure the geometric structure factor is an additional effect on the intensity of peaks that already satisfy the Bragg's scattering criterion ok.

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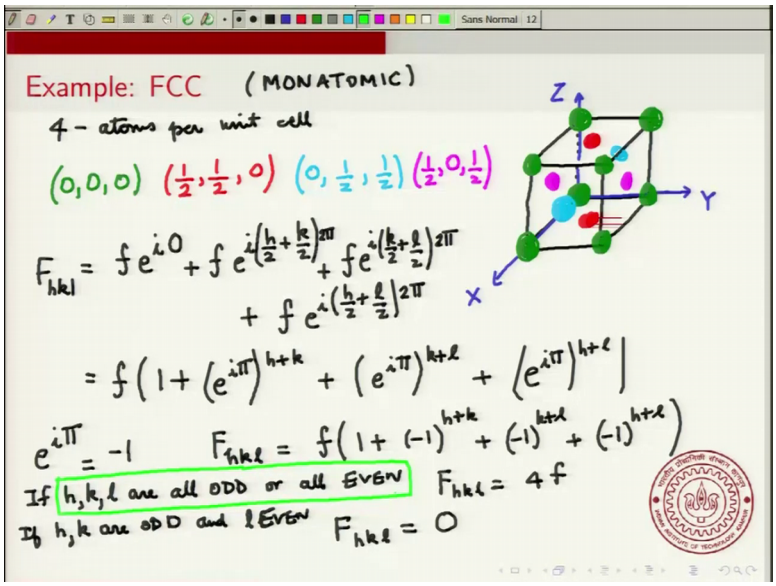

So, now let us take the example of FCC. So, in FCC there are 4 atoms per unit cell ok, and there are 4 atoms per unit cell. Now if you take the unique atoms unique atoms means not those that are related through a lattice translation. So, if I draw my ok. And let me take my origin, let me take my origin here, x, y, z. So, now, I am going to take the 4 unique atoms I am going to say are this one at this corner which due to lattice translation will be, due to lattice translation this same atom will appear at all the corners all the 8 corners.

So, I have the first atom at 0, 0, 0 which through lattice translations generates 8 other atoms ok. The next atom I will use a different color ok, which I will take it as right at this phase center ok, and this through lattice translation will generate another atom here and the coordinate of this atom is x the x coordinate is fractional coordinate is half, y fractional coordinate is half, the z fractional coordinate is 0 ok, and you can see the what are the remaining two atoms that I need to consider; I will consider one in the y, z plane that is write here at the center of this phase and that will be reproduce right in the center of this phase ok.

And this atom has coordinates of the x coordinate is 0, y coordinate is half, z coordinate is half ok. And I need to consider one more atom and that I will choose along the x, z; x, z x, z plane and that will be right here, this atom in purple, which will be translated due to translations it will also appear here, and the coordinate of this atom is half y

coordinate is 0, z coordinate is half ok. So, these are the four unique atoms, and we saw how with lattice translations they generate the entire FCC crystal.

So, the four atoms per unit cell are these and now let us calculate the geometric structure factor. So now, we can calculate f of h k l ok, this is given by now there will be an atomic form factor. Now if you take if you assume that this is a monatomic F FCC then all the atoms will have the same form factor. So, you will have f e to the i ok, now what is delta? For 0, 0, 0 delta is 0 ok, plus f e to the i. Now that the phase difference for this is half h h by 2 plus k by 2 ok and you can see you will have the phase difference for this is k by 2 plus l by 2 plus f e to the i h by 2 l by 2 ok.

Now e to the i times 0 is 1 and I have missed a factor of 2 pi there should be a 2 pi in each of these ok. And now e to the i times 0 is 1 ok. And let me just take f as a common factor and I have 1 plus now this h by 2 plus k by 2 into 2 pi is same as e to the i pi into raised to h plus k. And then I have e to the i pi raised to k plus l plus e to the i pi raised to h plus l. I have deliberately written it this way because I know that, e to the i pi, e to the i pi ok. This has cos pi plus i sin pi, sin pi is 0, cos pi is minus 1. So, this is equal to minus 1. So, therefore, you have f of hk l is equal to f times 1 plus minus 1 raised to h plus k plus minus 1 raised to k plus l plus minus 1 raised to h plus l ok.

So, you can see that if h, so if h plus k is odd, if h plus k is odd if h plus k is odd then this term will be minus 1 ok. If h plus k now if k plus l is all this term will be minus 1 and so on. If it is even if h plus case is even then this will be plus 1 ok.

So, now we can see that if h plus k k plus l h plus l are all even ok. If these sums are all even then each of these would be 1 and you will have a structure factor that is 4. So, and in fact, in fact if h plus k plus l are all odd or all even ok. If they are all odd or all even then, each of these sums h plus k k plus l and h plus l will be even ok. Then you will have f of h kl equal to 4 f and this is the condition for observing the peaks ok.

If h plus k if hk are odd and l even or vice versa or you can have h k or even and l odd ok, then you will see that that h and k are h and k are odd ok. So, h plus k will be even. So, it is sum of 2 odd numbers is an even number. So, h plus k will be even. So, this will be 1, but since k is odd and l is even k plus l will be odd. So, this will be minus 1. This will also be minus 1 h plus l will also be minus 1; so in this case you will get f equal to 0 ok.

So, basically what you will find is that, the condition for the peaks is that, h condition for observing the peaks is that. hkl should be all odd or all even ok. This is the condition for observing the peak in the diffraction pattern. So, even though, you may be satisfying Bragg's law ok; the values of h and k which are we in which in which they are not all odd or all even will not contribute will not show up in the X ray diffraction pattern. Now you can also do this for; so you can do this for different structures.

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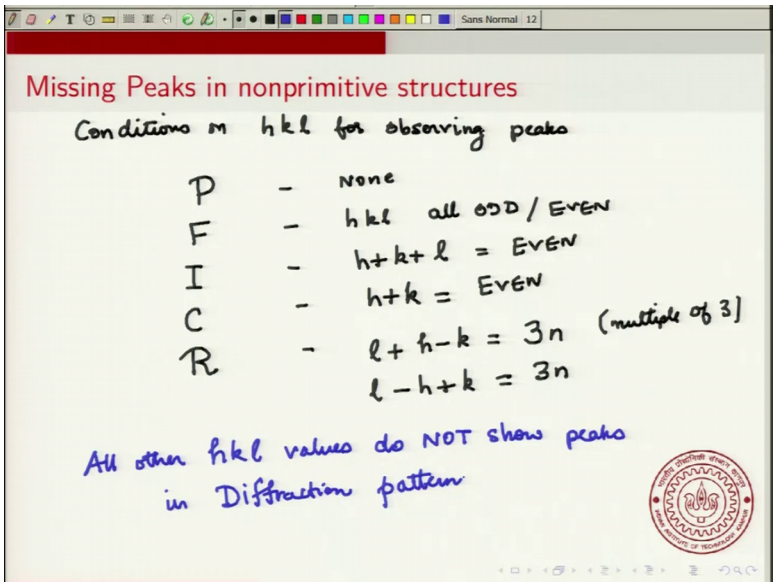

In general the condition for observing the peaks, condition on hkl for observing peaks ok; so this is for a primitive structure there is none. For a phase center we already saw that h k l all odd or all even ok. For a body centered cubic the condition is that h plus k plus l should be even. For C centered cubic ok, you have h plus k should be equal, should be even, and for a r center that is in the rhombohedral structures you have you have l plus h minus k equal to 3 is a multiple of 3, 3 n that is multiple of 3, of 3 or l minus h plus k equal to 3 n. So, only peaks that are observed are those where l plus h minus k equal to 3 n or l minus h plus k equal to 3 n.

So, I would expect you to know all these rules or because these are very quick, I mean if you know these rules you can quickly apply it to say whether the peaks are present or not. And so, all other peaks are missing in non primitive structures. So, all other all other hkl values do not show peaks in diffraction pattern.

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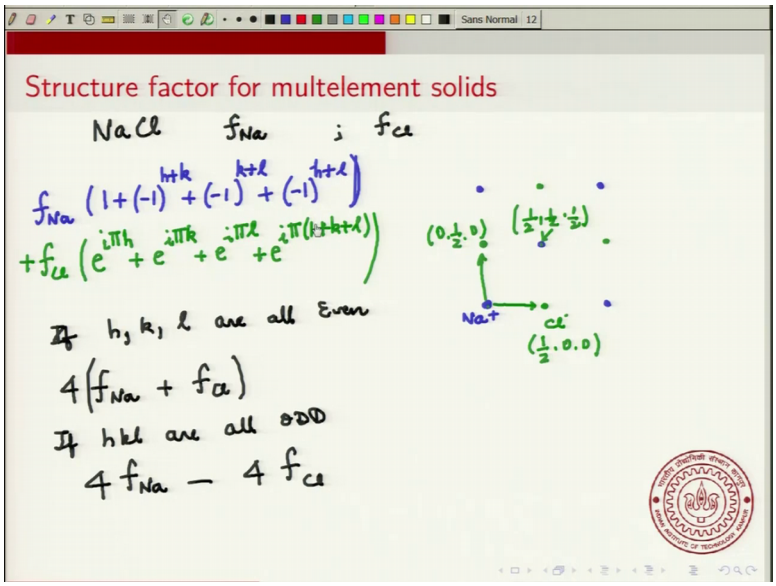

Now, before I conclude this lecture, I will just say that you can do this; you can also do this for multi element solids ok. So, let us take the example of NaCl. So, in NaCl you have you have a atomic form factor of Na and an atomic form factor of Cl ok. And now if you write the structure factor so ah, so let me draw the structure of NaCl.

So, I will draw Na in blue any atoms in blue. So, sodium atoms will form a phase centered, phase centered lattice and let me put the chloride, chloride ions the sodium ions will be in this phase centered lattice arrangement. The chloride ions will be at the at the x centers and the body center ok and also located at the body center ok. The body center will be located we will be located at some height of the screen ok.

So, the sodium atoms and these are the chloride ions. Chloride ions and sodium ions and now we can write the structure factor ok. I will not discuss this in detail, but you can see that you have f Na and now you have 8 atoms per unit cell f na into 1 plus again it will be just like what you had in the FCC h plus k pi or let me write it since we know this answer minus 1 raised to pi plus the minus 1 raised to h plus k plus minus 1 raised to k plus l plus minus 1 raised to h plus l, plus you will get the terms due to the chloride ions.

And here the chloride ions ok; so the location of the chloride ions is basically at you need to consider 4 4 of these chloride ions ok. One will be at the center of the cube at the body center ok. And the remaining three will be this, this and there will be one perpendicular

to the screen ok. That will that will come directly about this point ok, at the center of the phase that is at z equal to half and there will be about this at z equal to half ok.

So, so you can write the coordinates, now the first chloride atom is at will be at x equal to half y equal to 0. So, this is half 0, 0 and this is 0 half 0, the third one will be 0, 0, half and the fourth one will be at half, half, half ok. So, it will look like e to the i pi I have taken the factor of 2 and I will have h plus e to the i pi k plus e to the i pi l plus e to the i pi h plus k plus l ok. And this whole thing is multiplied by the form factor of chlorine ok. And you can analyze this for different values of h and k h k ln and then and you can find out what the peak will be.

So, for example, if h k l is all odd or all if h k l are all even ok, then each of these terms will be 1 ok. So, then the structure factor will be f Na. So, 4 f Na plus fcl and that will be the maximum of the intensity. Now if hkl are all odd then, the structure factor will be 4 f Na ok; so plus now in this case minus 4 f Cl ok.

So, because each of the each of these e to the each of the i pi h will be minus 1, e to the i pi k will be minus 1, e to the i pi l will be minus 1, e to the i pi h plus k plus l will also be odd, so that will also be minus 1 ok. So, you can do the structure factor for multi element solids in this way and you can generalize it to all kinds of solids. So, with this I will conclude the second lecture of week 9 and here we have seen how to calculate the geometric factor in detail ok.

Thank you.